Molecular and electronic structures of polythiomethylene (PTM)

Masaru Ohsaku and Hiromu Murata
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730, *Japan*

and Akira Imamura and Akitomo Tachibana
Department of Chemistry, Shiga University of Medical Science, Setatsukinowa-cho, Otsu, Shiga 520-21, *Japan*
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CNDO/2 calculations, using the tight-binding approximation for polymers, were applied to polythiomethylene (PTM) with *spd* and *sp* basis sets. The experimental conformational stability was well represented by the *spd* basis set but the *sp* basis set proved unsuccessful. The conformational stability of the PTM is discussed in comparison to that of polyoxymethylene (POM).

INTRODUCTION

Conformational analysis of polythiomethylene (PTM) has been carried out by vibrational spectra[1], X-ray analysis[2], and semi-empirical potential functions[3]. From experiment[1,2] it is recognized that the PTM molecule exists in a helical form, and this is well represented by calculations[3]. However, treatment by molecular orbital (MO) calculations has not yet been carried out. With oxygen analogues, such as polyoxymethylene (POM), X-ray analysis showed there are two stable conformations, orthorhombic (*O*POM)[4] and hexagonal (*H*POM)[5], while the conformational stabilities of *O*POM and *H*POM has been explained from the electronic–structural point of view[6].

Here, we have studied electronic structures of PTM by the CNDO/2 method[7], using the tight-binding approximation.[8]

METHOD

Calculations were carried out as in previous papers[6,9]. Geometries used were as follows: $r(\text{C–H}) = 1.09$ Å, $r(\text{C–S}) = 1.815$ Å, $\varphi(\text{CSC}) = \varphi(\text{SCS}) = 106°\ 52'$, and $\varphi(\text{HCS}) = 109°\ 59'$.

Here, the skeletal conformation of PTM can be described only by two torsional angles τ_1 and τ_2 as shown in *Figure 1*. The torsional angles used for the *TT*, *TG* and *GG* forms were 180°, 180°; 180°, 65° 59′; and 65° 59′, 65° 59′; respectively. Basis sets used were *spd* and *sp*.

RESULTS AND DISCUSSION

Table 1 shows the calculated total energies of the *TT*, *TG* and *GG* forms.

spd Calculation

The experimental conformational stability has been well represented by the *spd* basis set (*Table 1*), i.e. the order for calculated total energy is, $GG < TT < TG$. The differences between the *GG* and *TT* forms and between the *TT* and *TG* forms respectively are 0.35 eV (8.07 kcal) and 0.22 eV (5.07 kcal). This is enough to estimate the stable structure of PTM.

We now discuss the origin of the energy difference among the different conformations. Energy partitioning was carried out according to equations (1)–(4) of Ref 6:

Total energy, $GG < TT < TG$

Total intrasegment, $TG < TT < GG$

Total intersegment, $GG < TT < TG$

The *GG* form is destabilized by the intrasegment term, but stabilized by the intersegment term. The stabilization energy in the intersegment term adequately compensates for the destabilization in the intrasegment term. Therefore, this intersegment energy stabilizes the *GG* form more than the other forms of the PTM. This is quite different from the calculation for POM.[6] In helical POMs, *H*POM and *O*POM, the intrasegment term is smaller than in the *TT* form. However, in the intersegment term, the *trans* zigzag form is more stable than the helical forms.

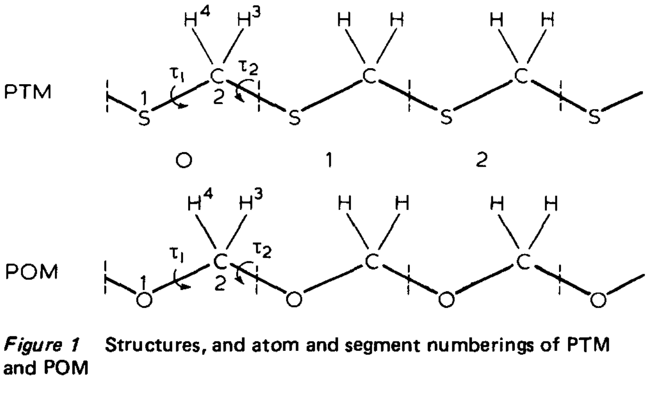

Figure 1 Structures, and atom and segment numberings of PTM and POM

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Table 1 Total energy (eV)/unit of PTM

Energy[a]	*GG* *spd*	*GG* *sp*	*TT* *spd*	*TT* *sp*	*TG* *spd*	*TG* *sp*
Total	–550.95	–537.11	–550.60	–537.29	–550.38	–537.22
Total intrasegment	–514.04	–514.70	–514.43	–514.62	–514.90	–514.67
Total one centre	–443.84	–451.03	–444.30	–451.10	–444.34	–451.11
Total two centre	–70.20	–63.66	–70.13	–63.52	–70.56	–63.57
Total intersegment	–36.92	–22.42	–36.18	–22.67	–35.48	–22.55
0–1[b] Total	–18.38	–11.21	–18.07	–11.31	–17.72	–11.25
Resonance	–18.31	–11.79	–18.09	–11.90	–17.81	–11.85
Exchange	–2.64	–2.01	–2.57	–2.00	–2.50	–1.99
Electrostatic	2.58	2.59	2.59	2.59	2.59	2.59
0–2 Total	–0.08	0.01	–0.02	–0.02	–0.02	–0.02
Resonance	–0.08	–	–0.01	–0.01	–0.01	–0.01
Exchange	–0.01	–	–0.01	–0.01	–0.01	–0.01
Electrostatic	0.01	0.01	–	–	–	–

[a] Meanings of the energy terms are shown in Ref 6

[b] For simplicity, 0–1 (segments) means the central and the first nearest neighbour segments, 0–2, 0–3, . . . refer to the central and the 2nd, 3rd, . . . nearest neighbour segments. In this article, up to 0–4 segments were taken into consideration for all polymers under study. Energy: the sign – means that absolute values are less than 0.01 eV. The 0–3 and 0–4 terms are not listed because the absolute values are less than 0.01 eV

Table 2 Electron density on the sulphur AO and total electron density on the sulphur atom in PTM

	GG *spd*	*GG* *sp*	*TT* *spd*	*TT* *sp*	*TG* *spd*	*TG* *sp*
s	1.73	1.69	1.71	1.70	1.71	1.70
p	1.01	1.35	1.07	1.34	1.23	1.45
	1.41	1.53	1.95	1.96	1.68	1.75
	1.29	1.48	0.71	1.02	0.82	1.13
d	0.11		0.25		0.21	
	0.16		0.19		0.13	
	0.18		0.09		0.14	
	0.13		0.05		0.09	
	0.13		0.08		0.09	
Total	6.14	6.05	6.09	6.03	6.10	6.04

This may be intimately related to the longer C–S bond length compared with the C–O bond. This will be discussed below, and is one of the most important findings presented here. With the intersegment terms, the difference appeared almost totally in the 0–1 and 0–2 terms.

Conformational analysis of the model molecules for PTM, such as $CH_3S(CH_2S)_nCH_3$ ($n = 1$–3), has been reported using vibrational spectra[10] and semiempirical[11] *spd'* CNDO/2 MO calculations[7]. For these model molecules the *GG* form is estimated to be the most stable form both by the observation[10,1] and by theory[11]. These results correspond well with our *spd* calculations for PTM.

sp Calculation

Calculations with *sp* basis sets were also carried out for comparison. The results are:

Total energy, $TT < TG < GG$

Total intrasegment, $GG < TG < TT$

Total intersegment, $TT < TG < GG$

Thus, the *sp* basis set cannot reproduce adequately the experimental conformational stability of PTM. The same is true of the model PTM molecule[11]. That is, *spd'* CNDO/2 calculations reproduce the experimental conformations for $CH_3SCH_2SCH_3$ and CH_3SCH_2SH but *sp* calculations do not.

We now discuss briefly the electron density on the sulphur atom in relation to the molecular conformations under the different basis sets, *spd* and *sp*. The electron density on the sulphur atom varied with the inclusion of the *d*-orbitals as shown in *Table 2*. From this we notice that the contribution of the 3*d* orbitals on the total density is about 10%. Reflecting this, the total energy of, for example, the *GG* form becomes noticeably different, –550.95 eV (*spd*) compared with –537.11 eV (*sp*). This energy difference comes mainly from three factors: (i) the difference in the one centre term in relation to the sulphur atom; (ii) the difference in resonance energy in relation to the S–C bond; and (iii) the difference in the intersegment (0–1) S...S resonance energy although the difference between the two sets is not as great:

GG form (eV/unit)	*spd*	*sp*
(i)	–31.87	–24.14
(ii)	–15.94	–12.08
(iii)	–1.65	0.11

The last term closely relates to the intersegment S...S bond order. From these results, therefore, we see that the *d*-orbitals play an important rơle in determining the molecular conformation of the organo-sulphur molecules.

Reproducibility of the torsional angles, τ_1 and τ_2

For the *GG* form of PTM, the total energy was estimated by varying the internal rotation angles τ_1 and τ_2 and fixing the other structural parameters. The total energy as a function of τ_1 and τ_2 is shown in *Figure 2*. From this, we can see only one minimum, around $\tau_1 = \tau_2 = 67.5°$, for the *spd* basis set. However, using *sp*, two minima appear in the calculations, although the barrier between these minima is very low. In this case, therefore, we can consider these as one. As a result the minima obtained by *spd* and *sp* calculations correspond with each

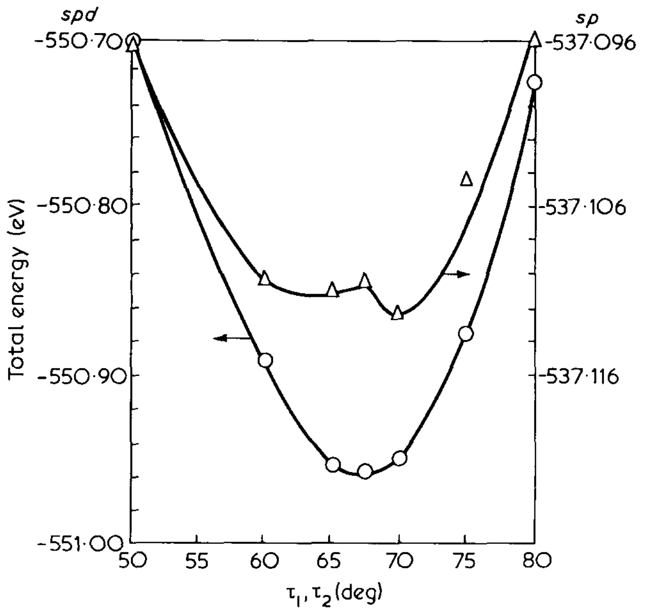

Figure 2 Total energy (eV) as a function of internal rotation angles τ_1 and τ_2 ($\tau_1 = \tau_2$) in PTM

other well, and these values excellently agreed with the experimental value, 65° 59′.[2]

Comparison of PTM with POM

We have attempted to clarify the difference between PTM and POM. To compare the molecular parameters of PTM with those of POM, bond angles φ(CXC) and φ(XCX) (X = O, S) are slightly wider in POM. The bond length r(C–X) is somewhat longer in PTM than in POM. However, the torsional angle of *H*POM is 76° 14′, and that of *O*POM is 63° 50′[4,5]. The torsional angle of *O*POM is nearly equal to that of PTM. Therefore, differences in the geometrical parameters of PTM and POM are condensed into (i) φ(CXC) and φ(XCX), and (ii) r(C–X). The differences may reflect the differences in the partitioned energies as described above. The difference in the valence angles may not bear upon the differences between POM and PTM. Therefore, differences in bond length should be responsible for the different results. The longer bond length in PTM diminishes the intersegment repulsion in the 0–1 segments compared with POM and the *GG* form is destabilized with respect to the *TT* form as shown below (eV/unit):

	*O*POM[6]	*Z*POM[6]	PTM *GG*	PTM *TT*
0–1 total	−13.85	−13.84	−18.38	−18.07
electrostatic	3.21	3.27	2.58	2.59
0–2 total	——	−0.03	−0.08	−0.02

Moreover in the 0–2 segments of the *GG* form in PTM fairly large values with minus sign appeared. The *GG* form increases in energy in the intersegment term. As a result, the *GG* form becomes the most stable in PTM. An analogous conclusion is drawn by statistical treatment[3].

CONCLUSIONS

The conformational stability of PTM has been explained by CNDO/2 calculations using an *spd* basis set; an *sp* basis set was found to be inadequate. The behaviour of the sulphur atom in PTM is different from that of the oxygen in POM.

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